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OFFICE OF NAVAL RESEARCH

Contract Nonr-1677(01)

Project No. NR-051-362

TECHNICAL REPORT NO. 7

Continuous Representations in the Statistical

Theory of Electronic Energies

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April 15, 1963

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Abstract

The use of continuous bases of representation other than a
plane-wave basis is considered in the theory developed originally by
Thomas and Fermi. The bases considered here are the sets of eigen-
functions of Hamiltonians corresponding to a particle subjected to a
field of force which varies inversely as the cube of the distance to
some fixed point. Variation of the strength of the interaction varies
the basis continuously. Calculations of the energy of the hydrogen
atom is carried out, with results that are appreciably closer to the
quantum mechanical result than is obtained with the original Thomas-
Fermi theory. Numerical results suggest the possible existence of a
statistical analogue of the Rayleigh-Ritz variation principle.

1. Introduction

The statistical theory originally introduced by Thomas[1] and Fermi[2] for describing the behavior of many-electron systems, had its origin in a quasi-classical statistical mechanical viewpoint which incorporated the Pauli exclusion principle. Subsequent investigations dealing with this theory have provided it with a better relation to quantum mechanical theory than it had originally. As a result, several modifications of the original Thomas-Fermi theory exist which incorporate features of a distinctly quantum mechanical character.[3] Of all of these, the "inhomogeneity correction" of von Weizsacker[4] has the most significant corrective influence upon the results obtained with the use of the statistical theory. Although this addition to the Thomas-Fermi theory was introduced originally in an ad hoc manner,[5] its presence, with slight modification from the original, seems assured from generalized treatments of the statistical method.[6]

However, in spite of any improvements which have been made on the original Thomas-Fermi theory, there remains one glaring deficiency in the theory: the density of electrons is either singular in the vicinity of a nucleus[7] or, on the basis of somewhat arbitrary auxiliary conditions, is set equal to zero.[8] It is to this aspect of the theory that the present paper is directed. The use of the momentum basis, traditionally associated with Thomas-Fermi theory, is a consequence of particular partitioning of the Hamiltonian operator. Here we address ourselves to the problem of alternative partitionings, preserving the spirit of the original theory by limiting ourselves to those partitionings that lead to continuous bases.

2. Formal Theory

In terms of a general formulation of the statistical theory based upon the use of the density matrix of many-electron systems,[9] the original Thomas-Fermi density may be derived entirely from the assumption that the kinetic energy and potential energy of a particle are commutable observables. This assumption, in fact, is basically the one made by both Thomas and Fermi. Such an assumption is illustrative of a certain type which generates a set of quasi-classical approximations.[10] For these approximations the Hamiltonian operator of the system is divided into two parts, the choice of the parts being a matter of convenience. The assumption that the two parts commute immediately produces an approximation to the density matrix which is the generalized analogue of the Thomas-Fermi theory.

In the interest of brevity, the formalism of (I) will be employed here. The density matrix (representative) of a many-particle system then may be expressed as[10]

$$\rho_M(x_1,x_2) = \sum_{n=1}^{\infty} \left\{ \theta(\lambda_M - \underline{H}) \psi_n(x_1) \right\}^* \left\{ \theta(\lambda_M - \underline{H}) \psi_n(x_2) \right\} , \qquad (2.1)$$

where $\underline{H}$ is the Hamiltonian operator of the system, $\left\{ \psi_n(x) \right\}$ is any properly symmetrised (i.e., with respect to exchange of identical particles) complete orthonormal set of functions of the correct boundary conditions. x stands for the entire set of configurational and spin coordinates of the particles, and λ_M is a parameter determined by

$$M = \mathrm{Tr}\, \rho_M = \int dx\, \rho_M(x,x) = \sum_{n=1}^{\infty} \left\langle \psi_n \,\middle|\, \theta(\lambda_M - \underline{H}) \,\middle|\, \psi_n \right\rangle . \qquad (2.2)$$

The spectral operator $\theta(\lambda_M - \underline{H})$ can be expressed most simply in terms of its matrix elements which are evaluated in a basis of eigenfunctions of $\underline{H}$. Then, we have for such a set $\left\{ \varphi_n(x) \right\}$ which satisfies

$$\langle \varphi_m | \underline{H} | \varphi_n \rangle = E_n \, \delta_{m,n} \tag{2.3}$$

the matrix elements

$$\langle \varphi_m | \theta(\lambda_M - \underline{H}) | \varphi_n \rangle = \theta(\lambda_M - E_n) \, \delta_{m,n} \tag{2.4}$$

with

$$\left. \begin{array}{l} \theta(y) = 1, \; y > 0, \\ \theta(y) = 0, \; y < 0. \end{array} \right\} \tag{2.5}$$

In these terms the "density" of the many-particle system in its configuration and spin space is given by $\rho_M(x,x)$, but corresponds to the density associated with the M lowest energy eigenstates of the system.[11]

The procedure to be exploited here involves making approximations to the Laplace transform of the density matrix defined in Eq. (2.1). For convenience, we may deal formally with the spectral operator and obtain[12]

$$\mathcal{L}\left\{\theta(\lambda - \underline{H})\right\} \equiv \int_0^\infty d\lambda \; e^{-z\lambda} \; \theta(\lambda - \underline{H}), \; \operatorname{Re}(z) > 0 \tag{2.6}$$

$$= \frac{e^{-z\underline{H}}}{z} \, . \tag{2.7}$$

As a consequence, a representation for the spectral operator is obtainable in terms of the inverse Laplace transform, viz.,

$$\theta(\lambda - \underline{H}) = \frac{1}{2\pi i} \mathcal{P} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{dz}{z} \, e^{z\lambda} \, e^{-z\underline{H}}, \; \operatorname{Re}(\gamma) > 0 \, . \tag{2.8}$$

Approximations which may be made for $\exp(-z\underline{H})$ give rise to approximations to $\theta(\lambda - \underline{H})$.

In particular, the quasi-classical approximation to which reference has been made arises as follows. Let.

$$\underline{H} = \underline{H}_o + \underline{H}_1(x) \tag{2.9}$$

and set

$$\exp(-\underline{a}\,\underline{H}) \doteq \exp(-\underline{a}\,\underline{H}_1)\, \exp(-\underline{a}\,\underline{H}_o)\,. \tag{2.10}$$

If we work directly in terms of a complete orthonormal basis of properly symmetrized eigenfunctions of $\underline{H}_o$, say $\left\{\,\mathcal{Q}_n^0(x)\,\right\}$, which satisfy

$$\langle\, \mathcal{Q}_m^0\,|\,\underline{H}_o\,|\, \mathcal{Q}_n^0\,\rangle = \underline{E}_n^0 \,\, \delta_{m,n} \tag{2.11}$$

we obtain the quasi-classical approximation to the density matrix

$$\left[\rho_M(x_1,x_2)\right]_{q.c.} = \sum_{n=1}^{\infty} \left\{\theta(\lambda_M - \underline{E}_n^0 - \underline{H}_1(x_1))\, \mathcal{Q}_n^0(x_1)\right\}^*$$

$$\times \left\{\theta(\lambda_M - \underline{E}_n^0 - \underline{H}_1(x_2))\, \mathcal{Q}_n^0(x_2)\right\}\,. \tag{2.12}$$

The preceding analysis is general and can be taken over in a single-particle approximation for a many-electron system. In such an approximation, $\underline{H}_o$ is an appropriate single-electron Hamiltonian and $\underline{H}_1$ is a suitable inter-action potential. The quantity M is taken equal to the number of single-electron eigenstates which, on account of spin degeneracy, is usually equated to half the number of electrons of the system.[13] In the Thomas-Fermi theory $\underline{H}_o$ is identified with the kinetic energy operator, $\left\{\mathcal{Q}_n^0(x)\right\}$ is a free particle basis and $\underline{H}_1(x)$ is a self-consistent potential which is deter-mined from Poisson's equation and certain physically plausible boundary conditions upon the potential. Regarding the latter, the condition that the potential has singularities corresponding to an attractive Coulomb field at any point immediately leads to a singularity there in the density. By con-trast, it will be noted, quantum mechanical solutions yield no such behavior for the density. As a result, the choice of a basis will be examined with the object of alleviating this difficulty in a quasi-classical approximation.

3. The Basis Functions

Because the object of the present paper is mainly constructive rather than analytical, no extensive analysis will be made of the seat of the aforementioned disparity in the density behavior. However, we may take note of the fact that for the systems generally of interest the binding energy is a finite quantity. This may be stated in more quantum mechanical terms as corresponding to a lowest finite eigenvalue of the Hamiltonian of the system. When measured relative to its lowest value, the eigenvalues of the Hamiltonian are non-negative as is, thus, the (modified) Hamiltonian itself. However, in the quasi-classical approximation which leads to the Thomas-Fermi theory, the Hamiltonian of a single particle is represented as the sum of two operators: the first is the kinetic energy and is non-negative while the second is the potential energy of the electron and is non-positive and can become unbounded for systems of interest. As a consequence, while the Laplace transform of the spectral distribution operator, Eq. (2.7), is a bounded operator in general, the approximation employed in Eq. (2.10) does not conform to this behavior.

Now, regardless of the choice of a non-negative $\underline{H}_o$ in Eq. (2.9), it is apparent from Eq. (2.12) that any negative singularity in $\underline{H}_1$ at, say,[14] $\vec{r}_K$, yields a divergent value for the density. To avoid this behavior, $\underline{H}_1$ must be chosen also to be bounded from below (i.e., $> -\infty$). For systems which involve only electrons and nuclei, the interaction between the particles involves only Coulomb terms which exhibit singularities that are simple poles. In any approximation of a self-consistent sort, we may suppose that no singularity of greater order need be introduced. Hence, specializing to a single-particle approximation, we wish to examine the possibility of finding $\underline{H}_o$ and $\underline{H}_1$ in Eq. (2.9) such that both are bounded from below. That is, letting

$$\underline{H} = \underline{T} + \underline{V} \text{ ,} \tag{3.1}$$

where $\underline{T}$ is the kinetic energy operator for an electron and $\underline{V}$ its potential energy function depending only upon its configurational coordinates, we seek a potential function such that

$$\underline{H}_0 = \underline{T} + \underline{V}_0$$

$$\tag{3.2}$$

$$\underline{H}_1 = \underline{V} - \underline{V}_0$$

are both bounded from below. Since $\underline{V}$ has no singularities other than simple poles, it is apparent that if, in the vicinity of the singularity $\vec{r}_K$,

$$V_0 \sim \frac{c}{|\vec{r} - \vec{r}_K|^s} \text{ ,} \quad s > 1 \tag{3.3}$$

with c a positive quantity, $\underline{H}_1$ will be bounded from below. Similarly, if $\underline{V}_0$ has the behavior exhibited in Eq. (3.3) with $s < 2$, $\underline{H}_0$ will also be bounded from below.[15] It is evident that a range of choices is possible for both c and s for the purpose at hand. Hence, considerations of convenience may be included in any final choice of $\underline{V}_0$.

In order to maintain some similarity to the original Thomas-Fermi theory, it is appropriate to deal with an $\underline{H}_0$ which admits only a continuum of positive eigenvalues. Such eigenvalues correspond to states for which the particle is unbound and is reminiscent of the free-particle basis of the Thomas-Fermi theory. At the same time it is desirable to have a $\underline{V}_0$ for which the minimum value of $\underline{H}_1$ has as small a magnitude as possible. Because the potential energy function $\underline{V}$ is to be kept general and unspecified, except for its singularities, a condition leading to fulfillment of this desire is impossible to formulate explicitly. Nevertheless, a certain choice of c and s in Eq. (3.3) will adequately fulfill the requirements which have been mentioned.

Consider the central field Hamiltonian

$$\underline{H}_0 = - \frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar^2}{8m} \frac{c}{r^2} \tag{3.4}$$

The value of c in Eq. (3.4) may range from zero to unity. The latter value
is the maximum which an attractive inverse square potential may have if the
ground state of the system is to be unbound. Any slight increase in the value
of the parameters yields a ground state energy value which corresponds to a
"fall" of the particle to the origin,[15] i.e., a negative infinite value of
the energy. Thus, the system corresponding to c = 1 in the Hamiltonian of
Eq. (3.4) is the limit of unbounded systems having an attractive center
varying inversely as some power of the distance from that center.[16] With
c = 0, the free-particle basis results.

Each Schroedinger equation corresponding to Eq. (3.4) generates a
complete, orthogonal and continuous set of functions which normalize accord-
ingly. Because of spherical symmetry of $\underline{H}_0$, the Schroedinger equation is
separable in terms of spherical polar coordinates. Hence, if

$$\underline{H}_0 \psi_{K\ell m} = E_{K\ell m} \psi_{K\ell m} \tag{3.5}$$

and

$$\psi_{K\ell m} = f_{K\ell}(r) \; Y_{\ell m}(\theta, \varphi), \; |m| \leqslant \ell = 0,1,2,\cdots, \tag{3.6}$$

where $Y_{\ell m}(\theta, \varphi)$ is a normalized spherical harmonic of the Eulerian angles
θ and φ[17], we obtain the radial equation

$$\frac{d^2 f_{K\ell}(r)}{dr^2} + \frac{2}{r} \frac{df_{K\ell}(r)}{dr} + (K^2 - \frac{\gamma}{r^2}) f_{K\ell}(r) = 0 \tag{3.7}$$

with

$$K^2 = \frac{2m}{\hbar^2} E_{K\ell m} \tag{3.8}$$

and

$$\gamma_\ell = \ell(\ell + 1) - c/4 \qquad (3.9)$$

With the transformation

$$R = Kr \qquad (3.10)$$

we obtain

$$\frac{d^2\left[R\, f_\ell(R)\right]}{dR^2} + (1 - \frac{\gamma_\ell}{R^2})\left[R\, f_\ell(R)\right] = 0 \qquad (3.11)$$

which is Bessel's equations. Its solutions yield

$$f_\ell(R) = R^{-1/2} J_{u_\ell}(R) , \qquad (3.12)$$

with

$$u_\ell = \pm \sqrt{(\ell + \tfrac{1}{2})^2 - c/4} \qquad (3.13)$$

and $J_u(x)$ is a Bessel function[18] of the first kind of order u.

For each $\ell \neq 0$ there is one value of u_ℓ which is positive and one which is negative. The latter correspond to solutions which diverge at the origin, while the former do not. Moreover, they diverge so strongly that the integral of the square of the eigenfunction over any finite volume enclosing the origin also diverges. Hence, they comprise unacceptable eigenfunctions. Thus, we shall take the positive sign in Eq. (3.13). For $c \neq 0$ the eigenfunction corresponding to $\ell = 0$ also diverges at the origin. However, the integral of its square over any finite volume enclosing it does not, so we retain it.[19]

Since the Bessel functions in Eq. (3.12) are not quadratically integrable, we examine the integral[20]

$$N_a(K_1,K_2) = \int_0^\infty dr\, r^2\, e^{-a^2 r^2}\, \frac{J_u(K_1 r)\, J_u(K_2 r)}{\sqrt{K_1 K_2}\ r}$$

$$= \frac{1}{2a^2 \sqrt{K_1 K_2}}\, e^{-\frac{K_1^2 + K_2^2}{4a^2}}\, I_u\!\left(\frac{K_1 K_2}{2a}\right) ,$$

where $I_u(x)$ is a Bessel function of the first kind of purely imaginary argument. From the asymptotic properties of the latter,[21] the dominant term is given by

$$I_u\left(\frac{K_1 K_2}{2a}\right) \sim \left(\frac{a^2}{\pi K_1 K_2}\right)^{\frac{1}{2}} \cdot e^{\frac{K_1 K_2}{2a^2}}$$

so that

$$\lim_{a^2 \to 0} N_a(K_1, K_2) = \frac{1}{2K_1 K_2} \left[\lim_{a^2 \to 0} \frac{e^{-\frac{(K_1-K_2)^2}{a^2}}}{(\pi a^2)^{\frac{1}{2}}} \right]. \qquad (3.14)$$

The term in brackets is a well-known representation of a delta function. As a consequence,

$$\int_0^\infty dK_1 \, K_1^2 \lim_{a^2 \to 0} N_a(K_1, K_2) = 1, \quad K_2 \neq 0 , \qquad (3.15)$$

and the original functions

$$\psi_{K\ell m} = \frac{1}{(Kr)^{\frac{1}{2}}} \, J_{u_\ell} (Kr) \, Y_{\ell,m}(\theta, \varphi) \qquad (3.16)$$

are properly normalized eigenfunctions of Eq. (3.5) in the sense of the integration of Eq. (3.16) which, together with Eq. (3.7), preserves the similarity with an integration over momenta as in the Thomas-Fermi basis.

4. The Quasi-Classical Density Matrix

The quasi-classical single-particle approximation to the density matrix now may be expressed in terms of the basis which has been described. Making use of Eqs. (2.12), (3.4), (3.8), (3.15) and (3.16), we obtain

$$\left[\rho_M(\vec{r}_1,\vec{r}_2)\right]_{q.c.} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \int_0^{\infty} dK \, K^2 \left[\left\{\theta(\lambda_M - \frac{\hbar^2}{2m}K^2 - \frac{\hbar^2}{8m}\frac{c}{r_1^2} - V(r_1))\right.\right.$$

$$\times \left.\frac{J_{u_\ell}(Kr_1)}{(Kr_1)^{\frac{1}{2}}} Y_{\ell m}(\theta_1,\varphi_1)\right\}$$

(4.1)

$$\times \left.\left\{\theta(\lambda_M - \frac{\hbar^2}{2m}K^2 - \frac{\hbar^2}{8m}\frac{c}{r_2^2} - V(r_2)) \frac{J_{u_\ell}(Kr_2)}{(Kr_2)^{\frac{1}{2}}} Y_{\ell m}(\theta_2,\varphi_2)\right\}\right].$$

With the aid of the Addition Theorem of Legendre polynomials,[22] the previous equation reduces to

$$\left[\rho_M(\vec{r}_1,\vec{r}_2)\right]_{q.c.} = \frac{1}{4\pi} \sum_{\ell=0}^{\infty} (2\ell+1) P_\ell\left(\frac{\vec{r}_1\cdot\vec{r}_2}{r_1 r_2}\right) \int_0^{\infty} dK \, K \, \theta_1 \, \theta_2 \frac{J_{u_\ell}(Kr_1) J_{u_\ell}(Kr_2)}{(r_1 r_2)^{\frac{1}{2}}},$$

(4.2)

where

$$\theta_j = \theta(\lambda_M - \frac{\hbar^2 K^2}{2m} - \frac{\hbar^2}{8m}\frac{c}{r_j^2} - V(r_j)).$$

The expression in Eq. (4.2) can be reduced further. However, we shall only do so for the diagonal elements of the density matrix, which correspond to the density. Making use of the properties of the θ-function, we obtain

$$\rho_M = \frac{1}{4\pi r} \sum_{\ell=0}^{\infty} (2\ell+1) \int_0^{K_M} dK \, K \, J_{u_\ell}^2(Kr)$$

(4.3)

where

$$K_M^2 = \frac{2m}{\hbar^2}(\lambda_M - V(r)) - c/4r^2 \geqslant 0.$$

(4.4)

Apart from the difference in the orders of the Bessel functions, the presence of the inverse square potential and a neglect of spin multiplicity, Eq. (4.3) is formally identical with the corresponding expression obtained in a

free-particle basis.[23]   Thus the terms corresponding to each value of

represent the contribution to the density made by particles having a square

angular momentum of $\ell(\ell + 1) \hbar^2$.

The approximation to the density given in Eq. (4.3) can be seen to

exhibit no divergence at the origin providing $V(r)$ exhibits no divergence as

strong as $1/r^2$. In cases of atomic systems, in which Coulomb forces apply,

this condition is satisfied. Because K_M vanishes then at some non-zero value

of r the density vanishes for all smaller values. While this behavior is

clearly unsatisfactory, it possibly represents a better approximation to a

finite density than is afforded by the original Thomas-Fermi theory. For

atomic systems we may anticipate that λ_M is negative. Thereupon, an asymp-

totic vanishing of $V(r)$ as $r \rightarrow \infty$ indicates the existence of a finite

distance beyond which the density vanishes identically. Thus, the density

given by Eq. (4.3) may be anticipated to have non-zero values in a limited

region of space.[24]

5. The Energy

The approximation which has been given for the quasi-classical

density matrix enables one to obtain an approximation for the energy. The

simplest way to do so is with the aid of the relation[25]

$$\langle E \rangle_M = \int_0^M \lambda_M \, dM = \lambda_M M - \int_{\lambda_o}^{\lambda_M} M \, d\lambda \, , \qquad (5.1)$$

where $\langle E \rangle_M$ is the sum of the first M eigenvalues. Since the quasi-

classical approximation, Eq. (4.2), involves λ_M through the spectral

operator, we need to examine

$$\int_{\lambda_o}^{\lambda_M} \theta\left(\lambda - \frac{\hbar^2 K^2}{2m} - \frac{\hbar^2}{8m}\frac{c}{r^2} - V(r)\right) d\lambda = \left\{\lambda_M - \frac{\hbar^2 K^2}{2m} - \frac{\hbar^2}{8m}\frac{c}{r^2} - V(r)\right\}$$

$$\times \;\; \theta\left(\lambda_M - \frac{\hbar^2 K^2}{2m} - \frac{\hbar^2}{8m}\frac{c}{r^2} - V(r)\right).$$

When combined with Eqs. (4.2), (4.3) and (5.1), there results the approximation

$$\langle E \rangle_M \doteq \int_0^\infty dr\, r\left[\sum_{\ell=0}^\infty (2\ell+1)\left\{\frac{\hbar^2}{8m}\frac{c}{r^2} + V(r)\right\}\int_0^{K_M} dK\, K\, J_{u_\ell}^2(Kr)\right]$$

$$+ \int_0^\infty dr\, r\left[\sum_{\ell=0}^\infty (2\ell+1)\frac{h^2}{2m}\int_0^{K_M} dK\, K^3\, J_{u_\ell}^2(Kr)\right]. \tag{5.2}$$

The last integral is the approximate expectation value of $\underline{H}_o$ given by Eq. (3.4) for the first M eigenvalues of $\underline{H}$. Both integrals can be reduced considerably with the aid of the Schafheitlin reduction formula for Bessel functions.[26]

The present approximation gives no indication of the reliability of the energy values, there being no extremum principle available to serve in this connection. However, since the eigenvalues satisfy the relation

$$\langle E^2 \rangle_1 = \langle E \rangle_1^2$$

$$\langle E^2 \rangle_2 = \langle E \rangle_1^2 + \left\{\langle E \rangle_2 - \langle E \rangle_1\right\}^2,$$

some estimate of the precision of the approximate energy values can be made. For this purpose, we must have an expression for the sum of the squares of the first M eigenvalues. We have

$$\langle E^2 \rangle_M = \int_0^M \lambda_M^2\, dM = \lambda_M^2 M + 2\int_{\lambda_o}^{\lambda_M} \lambda\, M\, d\lambda \tag{5.3}$$

Making use of Eq. (4.2) and carrying out the requisite operations, we obtain

$$\langle E^2 \rangle_M = \int_0^\infty dr\, r \left[\sum_{\ell=0}^{\infty} (2\ell + 1) \left\{ \frac{\hbar^2}{8m} \frac{c}{r^2} + V(r) \right\}^2 \int_0^{K_M} dK\, K\, J_{u_\ell}^2(Kr) \right]$$

$$- \int_0^\infty dr\, r \left[\sum_{\ell=0}^{\infty} (2\ell + 1) \frac{\hbar^2}{m} \left\{ \frac{h^2}{8m} \frac{c}{r^2} + V(r) \right\} \int_0^{K_M} dK\, K^3\, J_{u_\ell}^2(Kr) \right]$$

$$+ \int_0^\infty dr\, r \left[\sum_{\ell=0}^{\infty} (2\ell + 1) \frac{h^4}{4m^2} \int_0^{K_M} dK\, K^5\, J_{u_\ell}^2(Kr) \right]. \qquad (5.4)$$

With Eqs. (5.1) and (5.4) we are able to estimate the precision of the approximate energy values. Thus, for the lowest eigenvalue, M = 1 and $\Delta = \langle E^2 \rangle_1 - \langle E \rangle_1^2$ is a non-negative quality which vanishes for an eigenvalue. In the present approximation, Δ is a function of c, the strength of the inverse square potential. Hence, we may anticipate that some value of c may possibly render Δ a minimum. For such a value, the most precise value of $\langle E \rangle_1$ is obtained within the framework of the present theory.

6. Computational Techniques

The integration indicated in (4.3) may be performed explicitly, giving

$$\rho_M(\vec{r}) = \frac{r^2}{8\pi r^3} \sum_{\ell=0}^{\infty} (2\ell + 1) \left[J_{u_\ell}^2(X) - J_{u_\ell+1}(X)\, J_{u_\ell-1}(X) \right],$$

$$X = K_M r, \qquad (6.1)$$

where K_M is given by (4.4) and u_ℓ by (3.14). This expression is convenient for computational purposes. Obvious alterations give density expressions for the various energy terms considered in the last section.

The definition of density thus derived was applied to the problem of the hydrogen atom, for which $V(r) = -e^2/r$. An IBM 7090 Data Processing System was programmed to evaluate (6.1), together with (4.4) and (3.14), for various values of λ_M and c. In all cases, summations over ℓ were extended until further contribution was less than 1 part in 10^8 ($\ell \sim 7$). From the densities thus tabulated, normalization and energy integrals were evaluated, using Simpson's Rule. In each case, the expression under consideration was tabulated at a sufficient number of points so that further increase caused no significant change in the result of the integration. A typical mesh density was 50 points/Bohr radius. The energy expressions were evaluated and integrated in such a way as to allow the use of some of them as expectation values of inverse powers of r.

Several sets of calculations were performed. The equation $M(\lambda_M, c) = M_0$ was solved for λ_M at various values of c for $M_0 = 1$ and $M_0 = 5$, corresponding respectively to a filled 1s level, and filled 1s, 2s, and 2p levels, and energies and expectation values of powers of r were found for these values of λ_M and c. In addition, points on the curve $M(\lambda_M, c)$ vs. λ_M for c = 0.5 were found, so as to allow evaluation of

$$\int_0^{M_0} \lambda_M \, dM = \lambda_M M_0 - \int_{-\infty}^{\lambda_0} M \, d\lambda \qquad (6.2)$$

for $M_0 = 1$, where λ_0 is given by $M(\lambda_0, c) = 1$, the integration again being by Simpson's Rule. This constitutes a check on the numerical procedures, as the energy found in this way must agree with that found from the integration of the energy density at λ_0 and c . The number of points on this curve, 40, was not sufficient to give a result comparable in precision to the integration of the energy density, these calculations being used mainly to demonstrate the internal consistency of the results.

7. Numerical Results and Discussion

Table IA presents the results of calculations of the energy for $M = 1$. The most interesting feature of these results is the variation of $\langle E \rangle$ with c. As can be seen, $\langle E \rangle$ has a definite, though broad, maximum rather close to the quantum-mechanical value, suggesting the possible existence of a statistical analogue of the Rayleigh-Ritz variational principle. Similar behavior can be seen in Table IB, which gives results for $M = 5$. These quantities are shown graphically in Fig. 1a and 1b. Table IA also gives $\Delta = \langle E_1^2 \rangle - \langle E \rangle_1^2$, while a plot of Δ vs. c is shown in Fig. 2. There exists a value for c for which Δ is a minimum, though this does not coincide with the "best" value.[27] Also noteworthy is the great improvement in the energy over the value from the Fermi-Amaldi theory, with which these results are directly comparable, since the theories become identical for $c = 0$. Table IB also presents expectation values of various powers of r together with the Quantum Mechanical results and Fermi-Amaldi results. At $c = 0.6638$, corresponding to the "best" value of $\langle E \rangle$ there is a distinct improvement in all quantities. At $c = 0.95$, approximately the value corresponding to minimum Δ, the expectation values of the positive powers of r are estimated much less well. Presumably this is caused by the somewhat earlier cutoff in density attendant upon the use of $c > 0$. The removal of the infinity in the density at $r = 0$ is undoubtedly responsible for the improvement in the other quantities.

8. Future Applications

So far, we have constructed a generalized Thomas-Fermi single particle theory. Application to multiparticle systems may be achieved by invoking the idea of the self-consistent field. We may thus anticipate that the improvement in energies found here would be carried over into a

self-consistent field calculation. Such a series of calculations is in progress. Also, a molecular system of high symmetry is suitable for treatment in this way. This work is also in progress. Both will be reported on in due course.

Acknowledgements

Summary of Results for M = 1 (in Atomic Units)

c	λ	$\langle E\rangle_1$	$\langle E^2\rangle_1$	Δ	$\langle 1/r\rangle_1$	$\langle 1/r^2\rangle_1$	$\langle r\rangle_1$	$\langle r^2\rangle_1$
0.00	-.24038	-0.7211	∞	-	1.442	∞	1.541	3.205
0.50	-.24760	-0.5333	0.4458	.1614	1.067	2.414	1.543	3.117
0.60	-.25065	-0.5289	0.4170	.1373	1.058	2.239	1.528	3.048
0.6638	-.25310	-0.5280	0.4046	.1258	1.056	2.162	1.515	2.992
0.70	-.25470	-0.5283	0.3993	.1202	1.057	2.128	1.506	2.956
0.80	-.26040	-0.5325	0.3918	.1082	1.065	2.074	1.474	2.830
0.90	-.26940	-0.5455	0.3981	.1005	1.091	2.095	1.424	2.642
0.95	-.27705	-0.5596	0.4123	.0991	1.119	2.164	1.382	2.494
0.99	-.28920	-0.5857	0.4448	.1018	1.172	2.330	1.319	2.281
1.00	-.30105	-0.6139	0.4845	.1076	1.228	2.537	1.262	2.096
Quantum		-0.5000	0.2500	0	1.000	2.000	1.500	3.000

$\langle E\rangle_1$ at c = 0.50 from integration of (6.2) = -0.537.

Table IB

Summary of Results for M = 5 (in Atomic Units)

c	λ	$\langle E \rangle_5$	$\langle E^2 \rangle_5$
0.0	-0.08221	-1.2331	∞
0.3	-0.08248	-1.0711	0.6349
0.4	-0.08260	-1.0606	0.5647
0.5	-0.08273	-1.0559	0.5242
0.6	-0.08287	-1.0541	0.4933
0.7	-0.08303	-1.0578	0.4770
Quantum		-1.0000	0.3125

References

(1) L. H. Thomas, Proc. Cambridge Phil. Soc. <u>23</u>, 542 (1927).

(2) E. Fermi, Z. Physik <u>48</u>, 73 (1928).

(3) See, for example, P. Gombas, <u>Die Statistische Theory des Atoms und Ihre Andwendungen</u> (Springer-Verlag, Vienna, 1949).

(4) C. F. von Weizsacker, Z. Physik <u>96</u>, 431 (1935).

(5) See, for example, R. A. Berg and L. Willets, Proc. Phys. Soc. (London) <u>A68</u>, 229 (1955).

(6) See, for example, S. Golden, Phys. Rev. <u>105</u>, 604 (1957); see, also, G. A. Baraff and S. Borowitz, Phys. Rev. <u>121</u>, 1704 (1961).

(7) An early attempt to deal with this problem is that of W. J. Swiatecki, Proc. Phys. Soc. <u>A68</u>, 285 (1955).

(8) See, for example, J. M. C. Scott, Phil. Mag. <u>43</u>, 859 (1952), and R. A. Ballinger and N. H. March, Phil. Mag. <u>46</u>, 246 (1955).

(9) See, for example, S. Golden in Ref. (6).

(10) S. Golden, Phys. Rev. <u>107</u>, 1283 (1957), referred hereinafter as (I).

(11) This tacitly assumes that the energy spectrum is non-degenerate.

(12) One should use the two-sided Laplace transform, but with the tacit assumption that the Hamiltonian is measured from the lowest eigenvalue, the one-sided Laplace transform may be employed in the formalism.

(13) This tacitly assumes equal numbers of electrons in each spin state.

(14) We are restricting the following considerations to a single-particle approximation. Thus, $\vec{r}$ refers to the position vector of the particle.

(15) See, for example, L. D. Landau and E. M. Lifschits, <u>Quantum Mechanics</u> (Addison-Wesley Publishing Co., Reading, 1958), pp. 118-121.

(16) This basis may be termed the "barely-free-particle" basis.

(17) See, for example, Ref. (15), page 87.

(18) See, for example, G. N. Watson, <u>A Treatise on the Theory of Bessel Functions</u> (Cambridge University Press, Cambridge, 1948), p. 95.

(19) When c > 1 the order of the Bessel function for $\ell = 0$ is imaginary and diverges at the origin.

(20) Reference (18), p. 395.

(21) Reference (18), p. 203.

(22) Reference (15), p. 87.

(23) See, for example, S. Golden, Phys. Rev. 110, 1349 (1958).

(24) The same sort of behavior is imposed in an ad hoc manner in Ref. (6).

(25) Indicated in (I) and in S. Golden, Rev. Mod. Phys. 32, 322 (1960).

(26) Reference (18), p. 137.

(27) One must be hesitant about use of such a term as "best," since in the absences of both prior information as to the correct answer and a variational principle, no particular confidence can be placed in this value. The quantity, defined above, is a measure of significance.

FIG. 1a
$\langle E \rangle_1$ vs. C

FIG. 1b
$\langle E \rangle_5$ vs. C
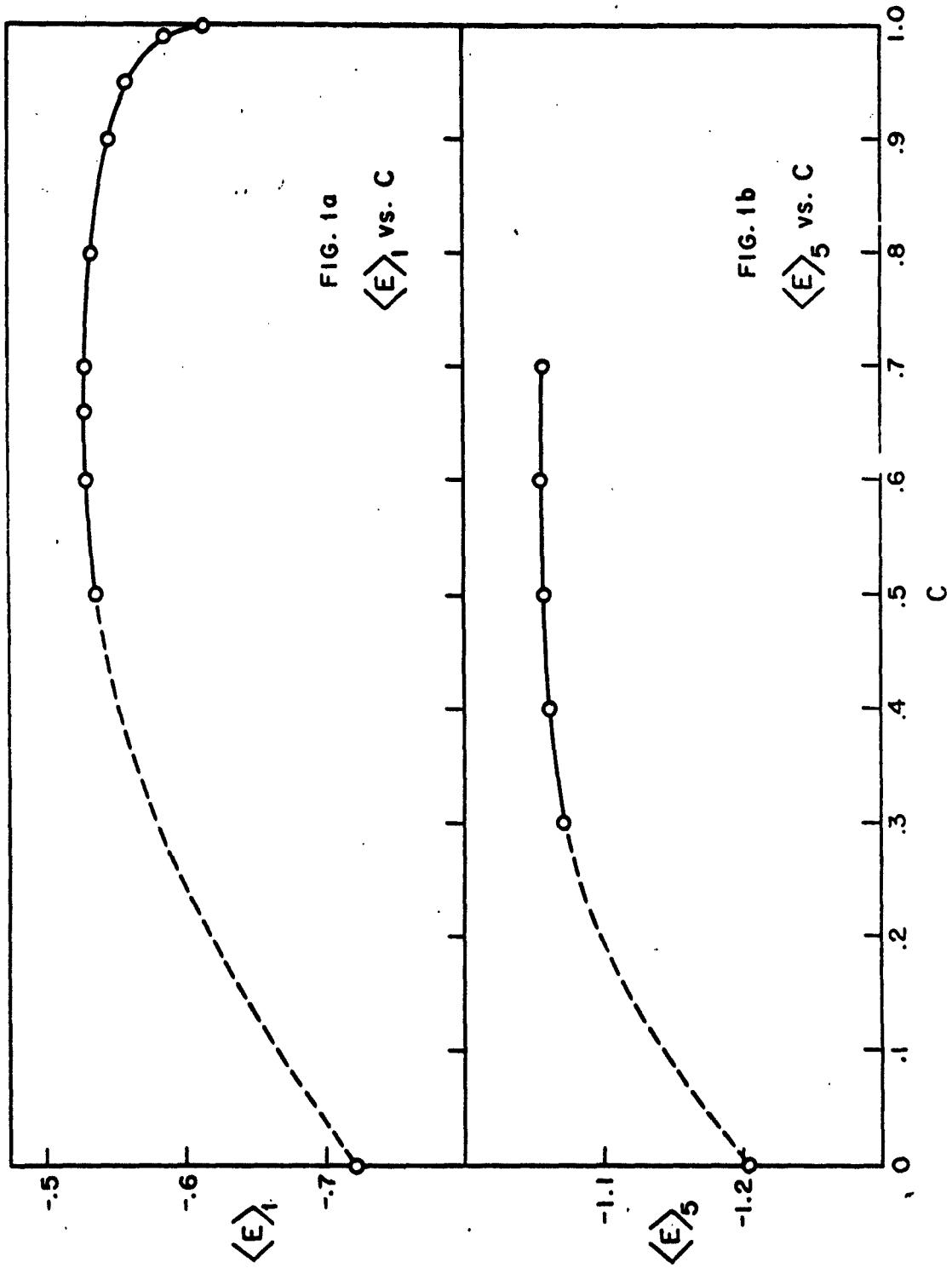
FIG. 2
Δ vs. C
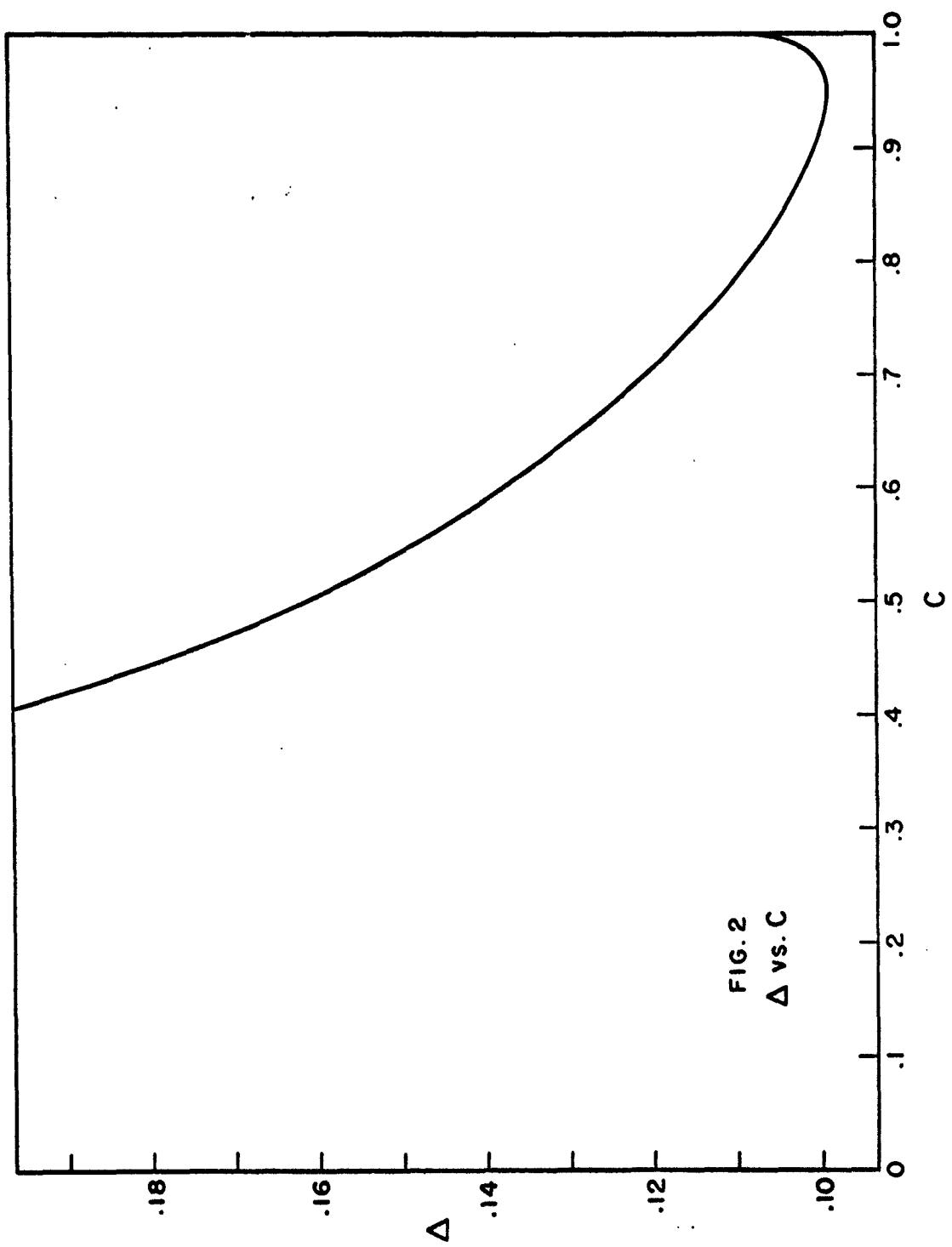
FIG. 3
RADIAL DENSITIES

Q. M.
T.F.A.
This work

$4\pi r^2 \rho(r)$

r/a_0
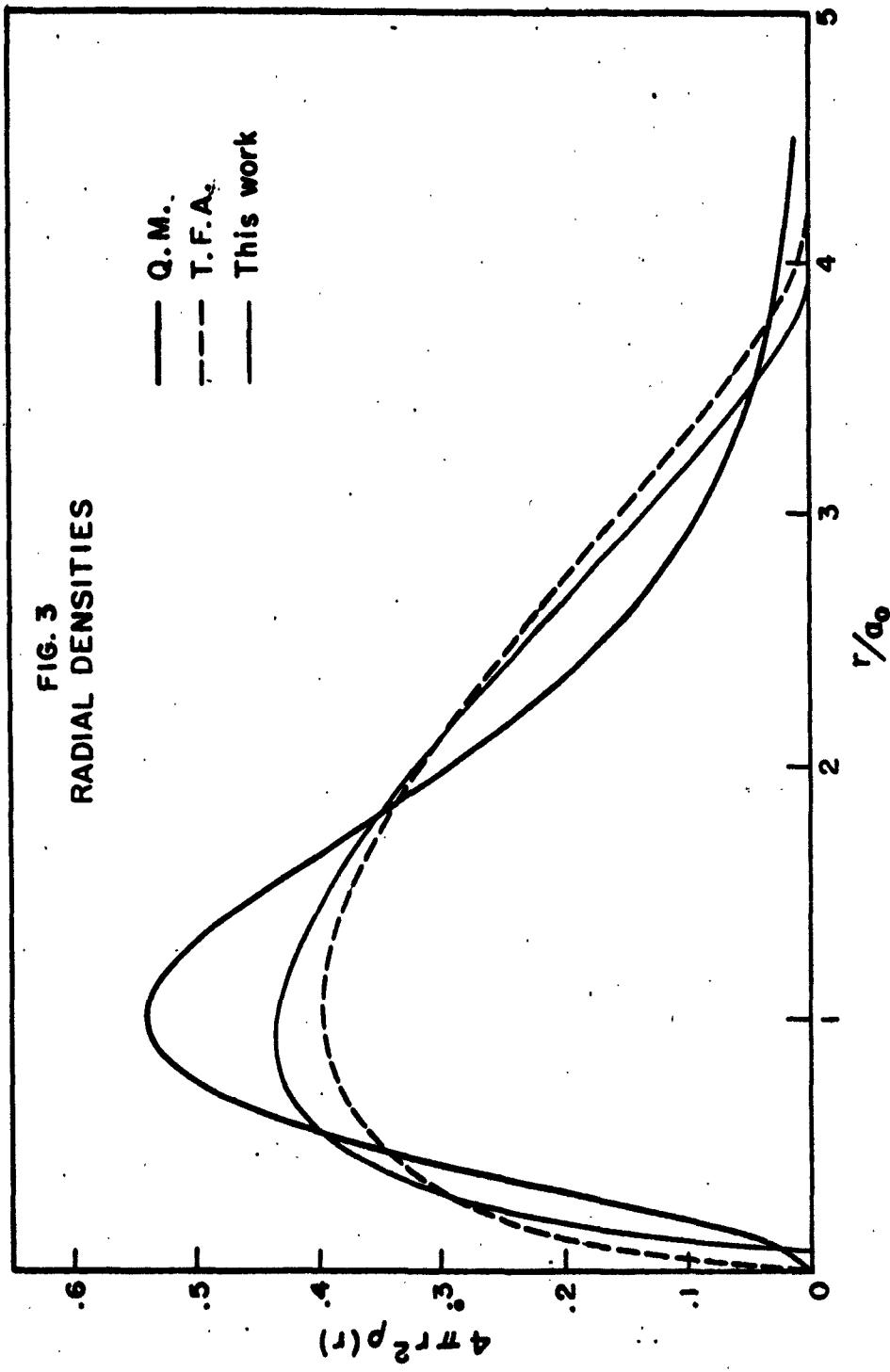
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